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SEPTEMBER 1954

WRIGHT AIR DEVELOPMENT CENTER

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MOLYBDENUM DISILICIDE COATING FOR GRAPHITE

INTRODUCTION

Ceramic materials are being developed and evaluated for use as components of uncooled rocket motors, in a program at Battelle for the Air Force. Of those materials that are commerically available, graphite has several outstanding properties for lining combustion chambers or exhaust nozzles. For example, graphite is extremely refractory, retaining its strength up to temperatures of about 4500 F. It has excellent resistance to thermal shock, a low specific gravity and, unlike most ceramics, it can be shaped by simple machining. However, its resistance to oxidation at elevated temperatures is poor and it is relatively soft, thus imposing the need for its protection before it can successfully withstand service in many rocket applications.

To improve its resistance to erosion, an investigation was made of molybdenum disilicide as a coating material and as an additive to the batch in preparing graphite bodies.

It is possible to produce a protective coating of molybdenum disilicide on graphite by vapor-phase deposition. However, to obtain uniform coatings on large complex shapes, such as some nozzles, the problems in control and equipment make this application technique questionable from a practical standpoint. For this reason, effort was devoted solely to the development of a coating by the more conventional method of heat treatment of a cold-applied slurry.

After establishing in the laboratory that it was possible to produce coatings in this manner, studies were made of variables in the process for the purpose of improving the coating and indicating critical variables for production control. Variables studied included the particle size and purity of the molybdenum disilicide powder, amount of resin in the vehicle, technique of cold application, type of graphite base, and time, temperature, and atmosphere of heat treatment. Appraisal of the coatings was made on the basis of visual observations and performance in a simulated rocket-nozzle test described in the Appendix.

BASIC COATING

From exploratory work, a basic coating composition and application method was developed for a selected graphite. This was used as the control in subsequent investigations of variables in the process, and is described below.

Materials

Molybdenum Disilicide ($MoSi_2$)

The molybdenum disilicide was obtained from Fansteel Metallurgical Corporation, North Chicago, Illinois. To prepare the compound, molybdenum powder, 99.9 per cent pure, and silicon powder, 97 per cent pure, are mixed in the stoichiometric ratio for $MoSi_2$, placed in molybdenum boats, and heated in a hydrogen atmosphere to about 1800 F. The powders react (exothermically) to form a porous, sintered briquet. Briquets were obtained for this work.

The purity of the as-received material was about 97 per cent $MoSi_2$, with aluminum, iron, copper, and calcium as the major impurities. A typical assay of the $MoSi_2$ is given below:

Element	Per Cent
Al	0.7
Fe	0.5
Cu	0.5
Ca	0.5
Ti	0.1
Ni	0.1
Mn	0.1
Mg, Cr, Zr Ag, Zn, W	Trace
$MoSi_2$	97.5 (by difference)

Comminution of the briquets was done in a 1-gallon rubber-lined mill. No special grinding balls were used. The mill was charged with the as-received briquets to about one-half of its volume. After about 8 hours of milling, the ground material was screened through a 325-mesh sieve. The portion retained on the sieve was returned to the mill, and more briquets were added for another mill charge.

The material which passed 325 mesh had an average particle size of 5 microns. Owing to its pyrophoric nature in the finely divided state, powdered $MoSi_2$ was stored in an air-tight glass container.

Vehicle

A thermosetting resin, designated as "79L", obtained from Ironsides Company, Columbus, Ohio, was employed as both a vehicle and a binder for the application of the $MoSi_2$ powder to the graphite. "79L" resin is a water solution of phenol-formaldehyde, containing about 65 per cent of resin solids. A coking value of 43 per cent was determined for the resin as received. A temperature of about 350 F was employed in this work to polymerize or harden the resin.

Graphite

ATJ grade graphite* was employed in the development of the basic coating. This grade of graphite was selected because of its fine-grained structure, good machinability, and high density. It is reported to have a maximum particle size of 0.0006 inch, and an apparent density of 1.70 to 1.75 g/cm^3. It is a molded graphite.

Coating Preparation

The composition of the basic coating was as follows:

Material	Parts by weight
Molybdenum disilicide powder, minus 325 mesh	91
"79L" resin solution, as received	9
Water	8

The disilicide powder was stirred into the resin-water solution to form a thin slurry of paintlike consistency. The composition was used immediately and not stored for reuse.

* Obtained from the National Carbon Company, Cleveland, Ohio.

Application

The graphite piece to be coated was first sanded lightly with fine-grained abrasive paper to clean and slightly roughen the surface. After sanding, loose particles were removed from the specimen by an air blast. The slurry was then applied to the surface by painting with an ordinary soft-bristle brush. No precise control of the coating thickness was employed in this exploratory work but, in general, applications were 15 to 30 mils in thickness. The slurry readily wetted the graphite, with a very rapid penetration of the vehicle into the surface. Coating thickness could be built up easily by successive applications. Frequent agitation of the slurry was required to prevent the powder from settling out of the vehicle.

Maturing Treatment

The green coating was air dried for at least 1 hour and then heated in air at 350 F for 30 minutes. This preliminary heat treatment polymerized the resin so that it formed a hard coating.

A carbon-resistor furnace was employed in maturing the coating. The design and operation of this is as described in a report prepared by Battelle under Air Force Contract No. AF 33(600)-5885 for the Materials Laboratory, Wright Air Development Center, and dated May 19, 1953. The report is titled "Design and Operation of a Carbon-Resistor Furnace".

A coated specimen was placed on a graphite setter and set in the hot zone of the furnace. Purified argon gas was employed as an atmosphere in the furnace. The gas, as received, was essentially 99 per cent pure with nitrogen as the major contaminant. A purification train removed oxygen, nitrogen, and water vapor from the gas before it entered the furnace. A continuous flow of the gas was metered into the furnace heating chamber at a rate sufficient to change the atmosphere about every 10 minutes. The furnace was purged for about 15 minutes prior to heat-up.

The specimens were heated from room temperature to about 3950 F in 1 hour and held at this temperature for about 15 minutes, and then were cooled with the furnace. Temperature measurements were made with an optical pyrometer sighted on the inner wall of the heater tube near the specimen.

LABORATORY APPRAISAL OF BASIC COATING

Visual observation, photomicrographs, and X-ray analyses were employed in the appraisal of the character and composition of the coating. A laboratory torch test was used for the evaluation of the protective quality of the coating.

Character of the Matured Coating

A glazelike surface was formed on the graphite when the coating was matured at 3950 F. The matured coating was dense, adherent to the graphite, and had a dark-gray, metallic appearance. During the maturing treatment, the coating melted and flowed over the graphite to provide a continuous surface.

X-ray-diffraction examinations of the matured coating showed the major phase and matrix to be an unidentified phase "X". An intermediate phase was identified as alpha silicon carbide (SiC). Molybdenum carbide (Mo_2C) also was identified as a minor constituent. These various phases are shown in Figure 1.

Adherence of the coating to the graphite apparently results from a reaction of the $MoSi_2$ with carbon at the elevated temperatures, forming SiC at the coating-graphite interface and "X" phase as a continuous matrix. A sectional view of a coated graphite specimen is shown in Figure 2.

The matured coating was about 3 to 5 mils in thickness when the slurry, as applied to the graphite, was 15 to 30 mils in thickness.

The X-ray pattern of the "X" phase, which was produced consistently in the matured coating, did not agree with any of the known X-ray patterns for Mo-Si, Mo-C, or SiC. An effort was made to produce a pure sample of "X" phase for analysis.

Compositions which ranged from 1Mo:2Si to 2Mo:1Si and carbon contents of 5 to 13 per cent were prepared as small pellets and heated from 3600 to 4000 F in an argon atmosphere. In no case was "X" phase produced as a single material; it was always accompanied by SiC and/or Mo_2C. Three of the heated compositions in this series of compositions were analyzed chemically. The results were as follows:

Prepared Composition	Chemical Analyses of Pellets Heated at 3800 F, per cent by weight			
	Mo	Si	C	SiC
$MoSi_2C_2$	56.0	30.0	10.0	27.0
MoSiC	73.0	21.5	5.8	9.0
MoSiC	72.8	14.9	3.0	7.7

From these data, the composition of "X" phase was calculated to be Mo_3Si_2C.

A study of the Mo-Si-C system by L. Brewer and O. Krikorian* shows a stable ternary compound, Mo_4Si_3C. From the results of these two separate investigations, it is concluded that the "X" phase developed in the coating is a molybdenum-silicon carbide.

Resistance to Torch Test

The matured coating imparted a protective surface to graphite when nozzle specimens were subjected to the high-velocity, hot gases of a laboratory torch test. The design of the test nozzle, the test apparatus, and the procedure of the test are given in the Appendix.

The degree of protection afforded a graphite nozzle specimen by the coating is shown in Figure 3. Under the test conditions used on the specimens in Figure 3, the uncoated nozzle was reduced to about one-half its normal size by oxidation. The protected nozzle maintained its original shape, although the coating was crazed and broken through to the graphite in the test. A thin film of silica was formed on the surface of the coating during the first firing cycle.

The results of torch tests on other coated graphite nozzles are summarized in Figure 4.

In the laboratory torch test, the temperatures of the coated surface of the graphite specimens ranged from 2900 to 3500 F. Failure was declared when a break-through of the coating was observed. Close observation of the specimens under test indicated that the following factors contributed to the failure of the coating:

(1) Nonhomogeneity of the coating material

(2) Nonuniformity of application

* Letter from O. Krikorian, Department of Chemistry and Chemical Engineering, University of California, Berkeley, California.

250X As Polished 80131

FIGURE 1. MATURED COATING ON GRAPHITE

Note:

1. Dark-gray crystals are alpha silicon carbide
2. Light-gray matrix is the "X" phase
3. Lighter gray crystalline material is molybdenum carbide
4. Black areas are voids or fissures

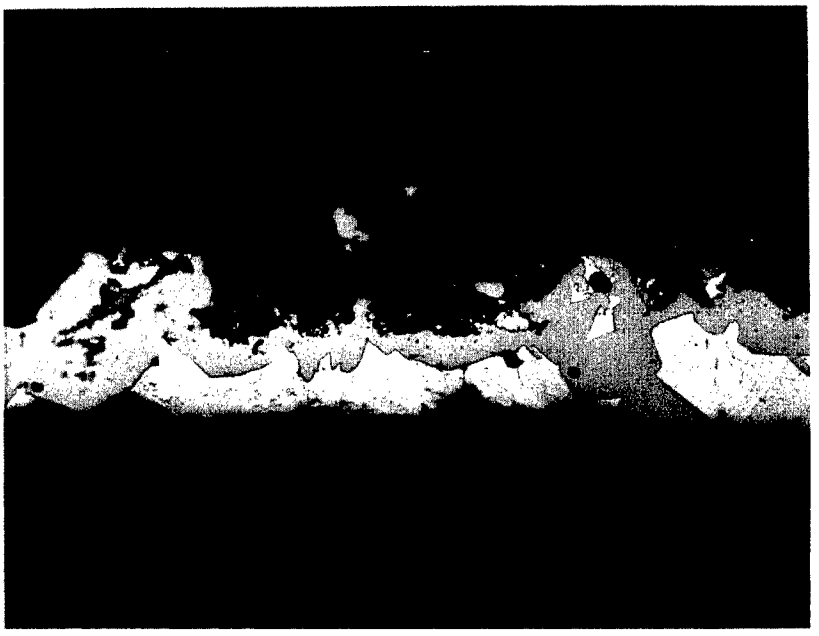

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FIGURE 2. A SECTIONAL VIEW OF THE COATING - GRAPHITE INTERFACE

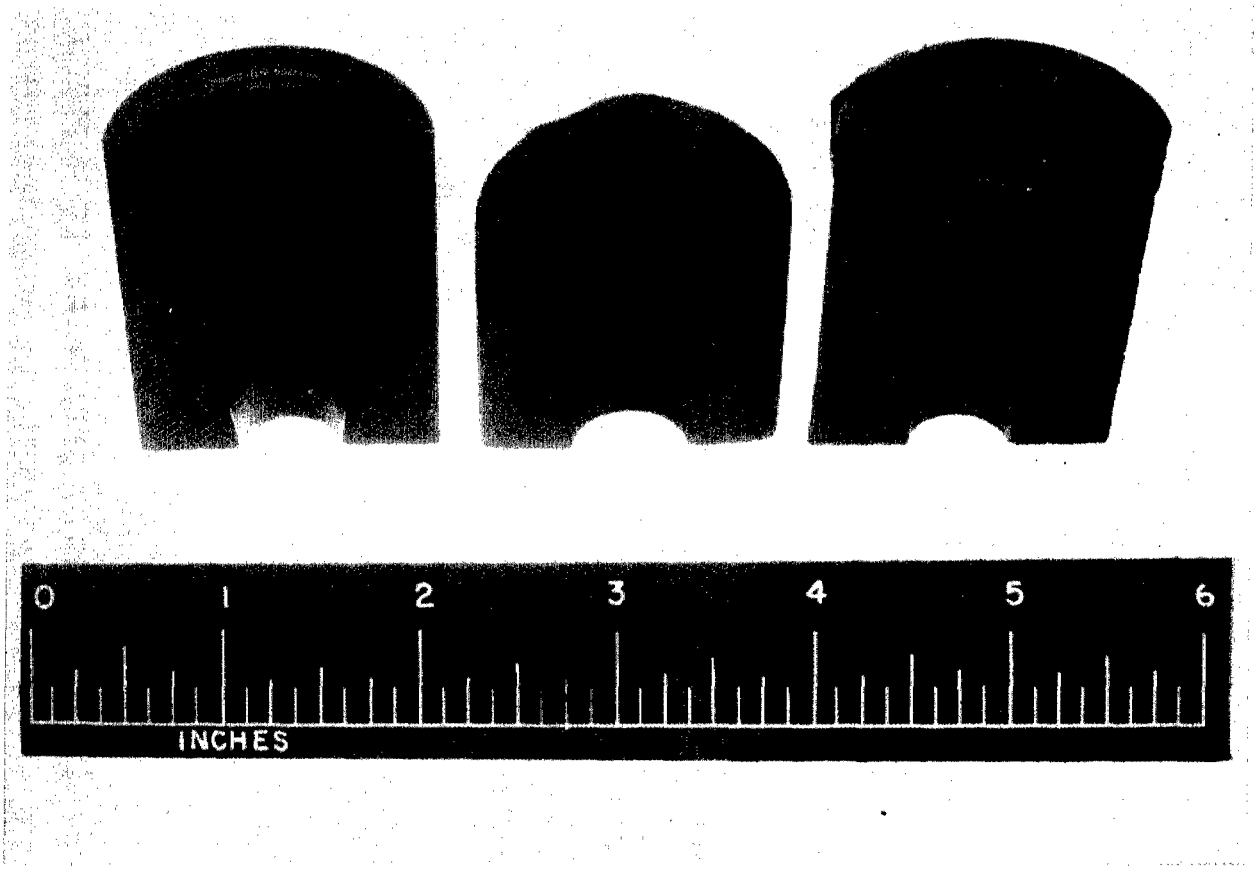

FIGURE 3. TORCH-TESTED SPECIMENS (SECTIONED)

Left: ATJ graphite, uncoated, not tested

Center: ATJ graphite, uncoated, tested for 10 firing cycles of 30 seconds' duration each in an oxymethane flame

Right: ATJ graphite, coated with $MoSi_2$ glaze and tested for 10 firing cycles of 30 seconds' duration each in the oxymethane flame

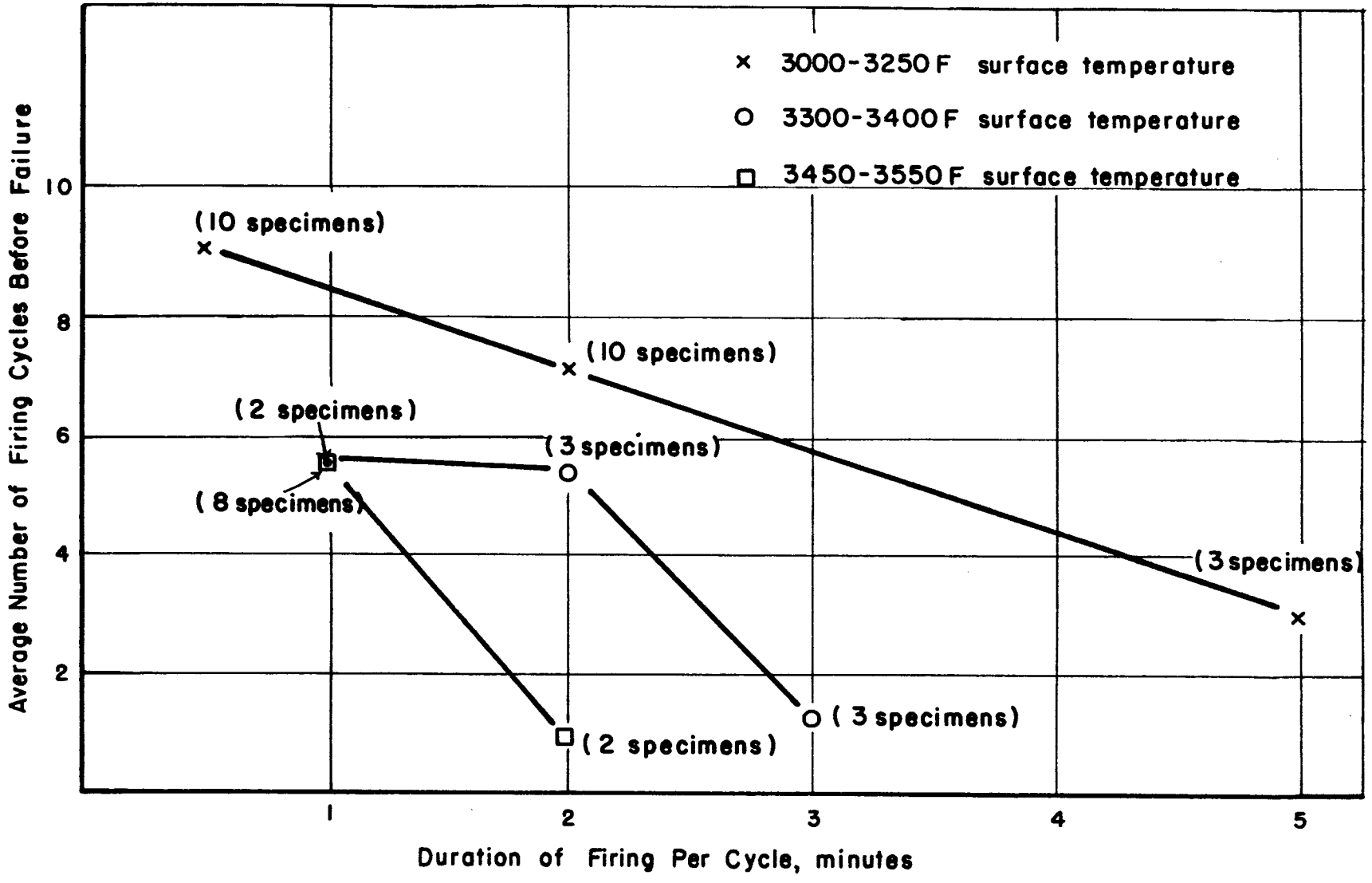

FIGURE 4. RESISTANCE OF COATED GRAPHITE SPECIMENS TO A CYCLIC TORCH TEST

A-11932

(3) Pinholes in the coating

(4) Crazing of the coating during cyclic firing

(5) Decomposition and/or melting of the coating when the surface temperature was greater than 3400 F.

An investigation of these various factors was made. The type of failures described in 1, 2, and 3 appeared to be reduced by the application of a double coating with subsequent maturing of the glaze after each application. X-ray analyses indicated a phase change in the coatings which were crazed during test. A volume change, coincident with this phase change, is an explanation for the crazing. The original coating before test was identified as two phases, a molybdenum-silicon carbide and SiC. After testing, $MoSi_2$ and SiO_2 were identified along with the original phases. The decomposition of the coating above 3400 F in an oxidizing atmosphere is an inherent property of the coating composition. At this elevated temperature, the rate of oxidation of the molybdenum-silicon carbide and SiC phases was appreciable. The SiO_2 product was readily removed in the gas stream of the torch test.

EFFECT OF PROCESSING VARIABLES ON COATING

Studies were made of the effect of processing variables on the basic coating, for the purpose of improving the coating and to indicate critical factors for production control. The variables investigated included the size and purity of the $MoSi_2$ powder, amount of resin in the vehicle, techniques of cold application, type of graphite base, and time, temperature, and atmosphere of heat treatment

The processing procedure just described for the basic coating was used in this study except when altered by the variable being investigated. Appraisal of the coatings was made on the basis of visual observations, X-ray analyses, and performance in the laboratory torch test. The results are given in the following sections.

Molybdenum Disilicide Powder

Coatings were prepared with $MoSi_2$ powders of minus 100-mesh, minus 270-mesh, and minus 325-mesh particle sizes. Some of the powders

as received from the manufacturer had a 97 per cent purity*. Other material used in this study was 99 per cent pure**.

All of the $MoSi_2$ powders produced coatings which were hard and adherent on the graphite, when matured at 3950 F. This study indicated that the quality of the coating is affected by the thickness to which it is applied. Control of the thickness depended on the uniformity of dispersion of the silicide in the resin vehicle which, in part, was related to the fineness of the powder and, in part, to the suspending power of the resin vehicle. Best results were obtained with a powder of 325 mesh or finer, as judged by ease of suspension in the vehicle, ease of application, and smoothness of the surface after maturing. Coarser grained powders of minus 100- or minus 270-mesh particle sizes were difficult to apply uniformly on the graphite and often produced discontinuous coatings when matured.

An attempt to substitute a cellulose gum for the phenol-formaldehyde resin normally used was not completely successful. The gum held the $MoSi_2$ powders in suspension and improved the application, but produced a low-density, porous coating after maturing.

Resin in Vehicle

Resin employed in the vehicle introduced carbon into the matured coating. A coking value of 43 per cent was determined for the "79L" resin, as received. Compositions containing various amounts of the resin were studied. Table 1 gives the character of these coatings and their resistance to the torch test.

The amount of carbon supplied by the resin had a marked effect. Fused, metalliclike coatings were obtained from the compositions prepared with 0 to 12 per cent of carbon. These coatings also were hard and adherent to the graphite. Discontinuous coatings were produced by the silicide powder in a resin-free water vehicle; they tended to crawl during the maturing treatment. This type of discontinuity was not apparent for the compositions containing carbon. Coatings with 15 and 30 per cent of the resin carbon had a dry, sintered appearance. The higher carbon content gave a soft, porous, nonadherent coating.

X-ray analyses of coatings prepared with 0, 4, 8, and 12 per cent of the resin carbon showed, in all cases, the major phase and matrix of the coatings to be the molybdenum-silicon carbide. The intermediate phase

* Fansteel Metallurgical Corporation, North Chicago, Illinois.

** American Electro Metal Corporation, Yonkers New York, and Electro Metallurgical Company, Niagara Falls, New York.

TABLE 1. EFFECT OF COATING COMPOSITION

Composition, parts by weight			Carbon Content in the Matured Coating[b], per cent by weight	Character of the Matured Coatings[c]	Resistance To Torch Test, number of firings before failure[d]	
Molybdenum Disilicide	"79L" Resin	Water[a] Addition			1 1/2-Minute Duration[e]	2-Minute Duration[f]
100.0	None	13.6	None	Hard, adherent, fused, and some discontinuity	1	4, 3, 1
95.4	4.6	10.6	2	Hard, adherent, fused, continuous	-	-
91.1	8.9	8.2	4	Ditto	9	7, 5, 2
87.0	13.0	5.6	6	"	-	-
83.2	16.8	2.9	8	"	5	2, 1
79.4	20.6	0	10	"	-	-
75.8	24.2	0	12	"	3	2, 1
70.9	29.1	0	15	Semihard, adherent, semifused, continuous	-	-
50.0	50.0	0	30	Soft, nonadherent, sintered, porous	1	< 1

(a) This amount of water maintained approximately the same fluidity for the various compositions.

(b) The calculated amount of carbon introduced in the matured coating as determined from the coking value of the resin.

(c) The various compositions were brushed-on specimens of ATJ graphite and matured at 3950 F in a carbon-resistor furnace employed an argon atmosphere.

(d) Failure was determined by the first apparent break in the coating.

(e) Maximum temperature of coating was measured as 3000 F.

(f) Maximum temperature of coating was measured as 3200 F.

was alpha or hexagonal SiC. Molybdenum carbide and carbon were present as minor phases. The structures of matured coatings prepared with 4, 8, and 12 per cent of resin carbon are shown in Figures 3, 4, and 5. The molybdenum-silicon carbide phase is indicated by the light-gray, continuous area, while the dark-gray crystals clearly show the hexagonal pattern of the SiC. The white or lighter gray particles are Mo_2C. The prominent black areas are considered to be voids or fissures, and the dark, minute particles are either carbon and/or SiC. The coatings prepared with 4 or 8 per cent of resin carbon, Figures 3 and 4, have fewer voids and larger SiC crystals than the coating containing 12 per cent of resin carbon. The coating with 12 per cent of resin carbon, Figure 5, shows a considerable amount of fine particles, considered to be free carbon. This fine material is not apparent in the coatings prepared with smaller amounts of resin carbon. The fissures which are apparent in all of the coatings appear to increase in size and amount with an increase in amount of resin carbon.

The phase analyses of the coatings applied with or without the resin in the vehicle indicate that the $MoSi_2$ takes carbon from the coating and/or the graphite base and is converted to carbide during the maturing treatment. The data also indicate that more than 12 per cent of resin carbon will provide undesirable free carbon in the coating.

Graphite nozzle specimens coated with compositions containing 0, 4, 8, 12, and 30 per cent of the resin carbon were subjected to cyclic blasts of high-velocity, hot gases in the torch tests. The results are given in Table 2. When exposed to blasts of 1/2- or 2-minute duration, the coating prepared with 4 per cent of the resin carbon had the best service life. Under the conditions of the test, the protective quality of the coatings containing higher amounts of carbon was significantly poorer. The coating prepared with no resin also was inferior in the torch test, as expected, in view of its discontinuous nature.

Method of Application

Methods for applying the $MoSi_2$ slurry on graphite investigated included dipping, spraying, and brushing.

The dipped coating was applied by immersing the specimen in the slurry for a period of 5 to 10 seconds, or sufficient time to obtain the desired coating thickness. The sprayed coating was applied with a commercial compressed-air spray gun. In all cases, the slurry readily wetted and adhered to the graphite, with very rapid penetration of the vehicle into the graphite. The thickness of the applied coating was easily built up by successive applications. Both the dipping and spraying techniques gave coatings with smooth surfaces. Brushing, however, usually produced a streaked or rough coating, resulting from the paint-brush bristles dragging over the surface of the specimen.

TABLE 2. PROTECTIVE QUALITY OF THE $MoSi_2$ COATING APPLIED BY VARIOUS TECHNIQUES

Method of Application[a]	Resistance To Torch Test, number of firings before failure[b]		
	1/2-Minute Duration[c]	1-Minute Duration[d]	2-Minute Duration[e]
Brushed, single application	9, 5	7, 6, 5	7, 5
Brushed, double application[f]	10[g]	7, 6	10[g]
Dipped, single application	10[g]	--	10[g], 9
Sprayed, single application	10[g]	8, 7	10[g]

(a) The coating slurry, as applied, was composed of 91 parts of molybdenum disilicide powder, minus 325 mesh, 9 parts of "79L" resin, and 8 parts of water. The coatings were applied 1/64 to 1/32 inch in thickness on nozzle specimens of ATJ graphite. The dried coatings then were matured at 3950 F for 15 minutes in an argon atmosphere.

(b) Failure of the coating was declared when a break-through to the graphite was observed.

(c) Maximum temperature of the coating was 3000 F.

(d) Maximum temperature of the coating was 3500 F.

(e) Maximum temperature of the coating was 3200 F.

(f) The coating was applied as described in Footnote (a) except that a second coat was applied over a matured base coat. The second coat was matured at 3750 F.

(g) No apparent failure of the coating.

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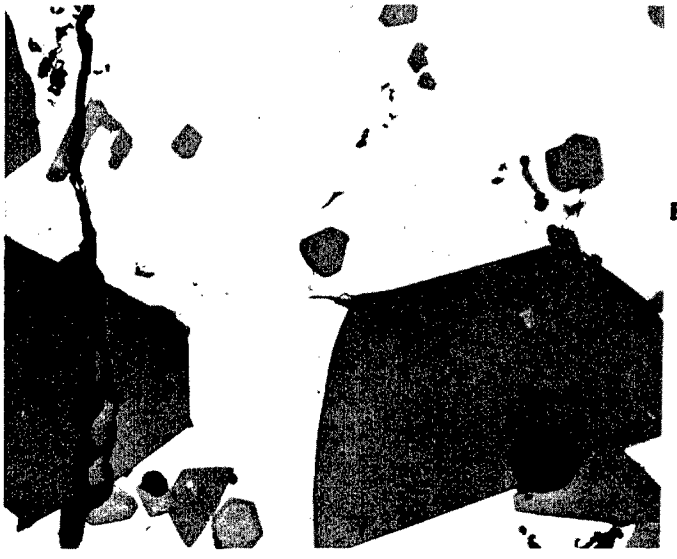
FIGURE 5. COATING PREPARED WITH 4 PER CENT CARBON



250X 80131

FIGURE 6. COATING PREPARED WITH 8 PER CENT CARBON

250X 80135

FIGURE 7. COATING PREPARED WITH 12 PER CENT CARBON

Surfaces As Polished

Coatings applied by the various techniques were evaluated in the laboratory torch test. The results are given in Table 2. Coatings applied by dipping, spraying, and a two-coat brushing had better resistance to the torch test than the normal single-coat brushing. In general, the coatings applied by these three methods sustained 10 cyclic blasts of 1/2-minute and of 2-minute duration without apparent failure; maximum surface temperatures were 3000 and 3200 F, respectively. Under the same test conditions, single, brushed-on coatings failed in less than 10 cycles. When tested in blasts of 60-second duration in which the surface temperature reached about 3500 F, the life of the coating, regardless of the method of application, was about 7 cycles. Under this more severe test condition, failure of the specimens was caused by oxidation and fusion of the coatings.

Various Graphites

Different graphite bodies obtained commercially or prepared in the laboratory were used as specimens for coating. ATJ, ATZ, and AGX grades of graphite were obtained from the National Carbon Company. The ATJ and ATZ graphite are comparable grades, possessing high strength and good machinability and having a fine-grained structure (0.006-inch maximum particle size). Their apparent densities are reported to be about 1.70 to 1.75 g/cm^3. The ATJ grade is formed by molding and the ATJ grade by extrusion. AGX grade is a common stock graphite having a maximum particle size of about 0.016 inch and an apparent density of about 1.55 g/cm^3; this grade can be obtained in either molded or extruded form. The extruded form was used in this work.

A Battelle graphite body, designated G, was developed primarily to permit molding the test specimen to shape rather than machining to shape as was done with the commercial graphites. This body had an apparent density of about 1.60 g/cm^3. Another Battelle body, GMS, was prepared with 35 per cent by weight of molybdenum disilicide powder and molded to shape; its apparent density was about 2.00 g/cm^3. The $MoSi_2$ was employed to promote adherence of the coating as well as to provide additional protection.

The compositions of the two laboratory-prepared graphite bodies are given below:

Material	Per Cent by Weight	
	Body G	Body GMS
Graphite powder, minus 200 mesh[a]	56	41
$MoSi_2$ powder, minus 200 mesh	0	27
Phenolic resin, alcohol solution[b]	44	32

(a) No. 2301 grade, obtained from The National Carbon Company.
(b) BV1600, a product of the Bakelite Corporation.

The respective compositions were mixed, dried, and crushed to a minus 35-mesh powder. Specimens were molded from this powder at a pressure of 15,000 psi, cured at 350 F, and then baked at 3700 F in an argon atmosphere.

The basic coating composition, previously described, was applied on these various graphite bodies by the brushing technique, and the specimens were matured at 3950 F.

In each case, the coating was hard, adherent, continuous, and metallic in appearance. The results of torch tests of nozzle specimens are given in Table 3. The protective quality of the coating was about the same for each of the commercial graphites, but was inferior when applied to the Battelle graphite body, G. However, the coating on the Battelle body containing the internal addition of $MoSi_2$ was equivalent to the coated commercial bodies in the test, indicating that an internal addition of $MoSi_2$ is beneficial.

Maturing Temperature and Time

The maturing range for the basic coating composition was investigated. Results are given in Table 4.

The character and structure of the coating changed when specimens were matured at 3600 to 4300 F. The coating was granular at 3600 and 3700 F. In the range of 3800 to 4100 F, the coating had a fused, metallic appearance. Above 4100 F, the coating was fused and highly crystalline. The crystals were identified as SiC; their development with temperature is shown in Figures 8, 9, 10, and 11. Decomposition of the coating was apparent when matured at 4300 F. In general, the coatings were hard and adherent to the graphite at all of the maturing temperatures studied.

X-ray analyses of the coatings indicated that they had the structure previously described, in that molybdenum-silicon carbide, SiC, and Mo_2C were identified. For the range of maturing temperatures studied, the relative intensity of the Mo_xSi_y C and SiC phases increased from medium strong to strong with increasing temperature. Molybdenum carbide was identified only in the coatings that were matured at 3800 and higher; its intensity in relation to the other two phases was faint.

When specimens were heated at 3950 F for periods of 0, 5, 10, 15, 20, or 25 minutes, the character of the fused, metalliclike coatings was not altered appreciably.

TABLE 3. PROTECTIVE QUALITY OF THE $MoSi_2$ COATING ON VARIOUS GRAPHITE BODIES[a]

Type of Graphite Bodies	Method of Forming	Bulk Density, g per cm^3	Resistance to Torch Test, number of firings before failure[b], 2-Minute Duration
ATJ grade, National Carbon Company[c]	Molded	1.70-1.75	7, 5
ATZ grade, National Carbon Company[c]	Extruded	1.70-1.75	7, 4
AGX grade, National Carbon Company[c]	Extruded	1.55-1.60	7, 3
Battelle-developed body, G[d]	Molded	1.55-1.60	3, 1
Battelle-developed body containing 35 per cent of molybdenum disilicide[d], GMS	Molded	about 2.00	7, 2

(a) The coating, as applied, was composed of 91 parts of molybdenum disilicide powder, minus 325 mesh, 9 parts of "79L" resin, and 8 parts of water. The coating was brushed on nozzle specimens to a thickness of 1/64 to 1/32 inch. The coated specimens were matured at 3950 F for 15 minutes in an argon atmosphere.

(b) Failure of the coating was declared when a break-through to the graphite was observed.

(c) Nozzle specimens were machined to shape.

(d) Nozzle specimens were molded to shape.

TABLE 4. EFFECT OF MATURING TEMPERATURE ON THE $MoSi_2$ COATING[a]

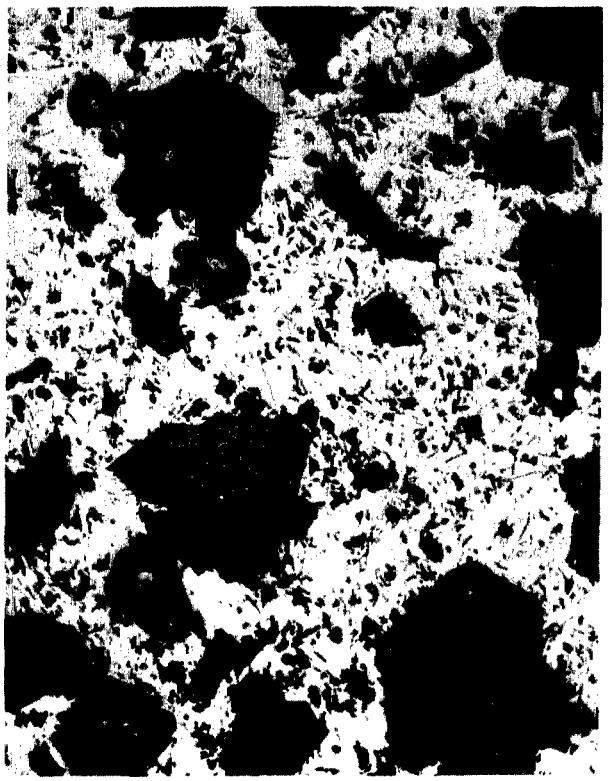
Maturing Temperature[b], F	Observed Character of the Coating	X-Ray-Diffraction Analysis, Relative Intensity of Identified Phases: Molybdenum-Silicon Carbide	Silicon Carbide	Molybdenum Carbide	Resistance to Torch Test, number of firings before failure[c]: 2-Minute Duration
3600	Hard, adherent, sintered, granular	Medium strong	Medium strong	None	7
3700	Ditto	Ditto	Ditto	"	6
3800	Hard, adherent, semifused, metallic	"	"	Faint	4
3900	Hard, adherent, fused, metallic	"	Strong	"	5
4050	Ditto	Strong	"	"	6
4100	"	"	"	"	6
4150	Hard, adherent, fused, crystalline	"	"	"	7
4250	Ditto	"	"	"	4
4300	Hard, adherent, highly crystalline, some decomposition	"	"	"	-(d)

(a) The coating, as applied, was composed of 91 parts of molybdenum disilicide powder, minus 325 mesh, 9 parts of "79L" resin, and 8 parts of water. The coating was brushed on nozzle specimens of ATZ graphite in a 1/64 to 1/32-inch thickness.

(b) The coated specimens were matured at the respective temperatures for 15 minutes in an argon atmosphere.

(c) Failure of the coating was declared when a break-through to the graphite was observed.

(d) The coating was discontinuous and was not tested.



250X As Polished 80129

FIGURE 8. COATING MATURED AT 3800 F

250X As Polished 80130

FIGURE 9. COATING MATURED AT 3900 F

250X As Polished 80131

FIGURE 10. COATING MATURED AT 4000 F

250X As Polished 80132

FIGURE 11. COATING MATURED AT 4100 F

The resistance of the coatings to high-velocity, hot gases of the torch test was independent of maturing temperature when the specimens were matured in the range of 3800 to 4200 F.

Furnace Atmosphere

Both the rate of flow and composition of the gas in the furnace used for maturing the coating were investigated. To study oxygen contamination primarily, various ratios of air and argon were introduced into the furnace used for processing the basic coating. For part of this study, specimens were heated in the static atmosphere of an induction furnace. To study the effect of flow rate, the usual carbon-resistor furnace was used.

Table 5 gives results of the investigation. The amount of air contamination in the argon was not so critical in producing sound coatings as was the rate of flow across the specimen in the maturing treatment.

Hard, adherent, continuous coatings were obtained when the specimens were matured in static argon containing 0, 10, 15, or 50 per cent by volume of air using the induction furnace. A similar result was obtained when specimens were heated in a static atmosphere in the carbon-resistor furnace. In this case, the furnace was purged only with argon prior to heat-up.

In the study of moving argon atmospheres, good coatings were produced when specimens were protected from the direct impingement of the flowing gas, or when the flow rate was less than nine changes of furnace atmosphere per hour. When specimens were exposed to flow rates of argon, ranging from 9 to 55 changes of atmosphere per hour, the matured coatings were discontinuous in varying degrees. The amount of disruption of the coating increased with increasing flow rates. Spectrographic and chemical analyses of the coatings showed that the silicon-molybdenum ratio was lower in the disrupted areas than in the good areas. Discontinuous coatings also were produced when an air atmosphere was introduced into the furnace at rates of 3 to 25 changes per hour.

Other gases were investigated to determine their utility as an atmosphere in which the $MoSi_2$ coating could be matured successfully. Helium, as received, was satisfactory in producing good coatings. Nitrogen, when used as received, caused some disruption of the coating. However, when the gas was purified by passing it over hot copper turnings to remove oxygen and then through a drying chamber to remove water vapor, good coatings were obtained.

TABLE 5. EFFECTS OF FURNACE ATMOSPHERE ON MATURING OF $MoSi_2$ BASE COATING[a]

Atmosphere Introduced Into Furnace, per cent by volume		Flow Rate of Atmosphere, changes per hour	Heating System	Observed Character of Matured Coatings
Air	Argon			
0	100	Static	Induction furnace, sealed	Hard, adherent, continuous, bright metallic
5	95	"	Ditto	Ditto
10	90	"	"	"
15	85	"	"	"
50	50	"	"	Hard, adherent, continuous, dull metallic
--	--[b]	"	Carbon-resistor furnace	Ditto
100	0	3	Ditto	Discontinuous coating
100	0	9	"	Ditto
100	0	25	"	"
0	100	3	"	Hard, adherent, continuous, bright metallic
0	100	9	"	Discontinuous on leading end of specimen
0	100	18	"	About 50 per cent of coating was discontinuous from leading end
0	100	55	"	Discontinuous coating
0	100	55[c]	"	Hard, adherent, continuous, bright metallic

(a) A paint composed of $MoSi_2$ powder, minus 325 mesh, in an aqueous solution of a phenol-formaldehyde resin, "79L" was applied to ATJ grade graphite specimens and matured at 3950 F for about 15 minutes.

(b) The furnace was purged for 1/2 hour with argon prior to heat-up. No gas was introduced during the maturing treatment.

(c) Specimens were enclosed in a graphite crucible and not exposed to the introduced atmosphere.

ROCKET-MOTOR TESTS OF COATED GRAPHITE LINERS

Graphite nozzle and combustion-chamber liners protected with the basic coating were evaluated in rocket-firing tests at Bell Aircraft Corporation and Wright-Patterson Air Force Base. In these tests, the coating gave considerable protection to the graphite liners from high-velocity, hot exhaust gases of uncooled, liquid-propellant motors. No details of the test conditions or results are included in this unclassified report for security reasons. The test results are given in the following classified reports:

(1) "Ceramic Liners For Rocket Thrust Chambers"
Report No. 56-982-015
October 31, 1952
W. R. Sheridan
Bell Aircraft Corporation
Buffalo, New York

(2) "Evaluation and Test of Ceramic Materials in Rocket Engine Thrust Chambers"
Technical Note WCLP 53-313
December 1953
Lt. L. T. Fuszara and Lt. J. J. Krochmal
Power Plant Laboratory
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

CONCLUSIONS

Molybdenum disilicide powder dispersed in a resin vehicle forms a hard, adherent, glazelike coating when applied to graphite and heated at elevated temperatures in a neutral or reducing atmosphere. The coating provides considerable protection for graphite when exposed to high-velocity, hot, oxidizing gases. Its service life, of course, varies with the severity of the operating conditions. The upper temperature limit of the coating under oxidizing conditions is 3500 F.

To produce sound coatings, the following control measures are needed:

(1) The $MoSi_2$ powder should be at least 97 per cent pure, and minus 325 mesh in size.

(2) The vehicle should not introduce more than 10 per cent of carbon into the coating.

(3) Both spraying and painting methods can be used to apply the coating, with spraying recommended for large shapes.

(4) The maturing temperature should be about 3900 F, with a maturing range from 3800 to 4000 F.

(5) The heat-up rate in the maturing treatment can be rapid: 45 minutes to temperature was employed successfully in laboratory heats. The time at maturing temperature for sound coatings will vary from 5 to 15 minutes depending on the size of the piece.

(6) A furnace atmosphere which is neutral or reducing is required for the protection of the ware and the furnace elements from oxidation.

(7) The piece has to be protected from direct impingment of a flowing furnace atmosphere. Impingement causes a disruption of the coating.

Using these processing conditions, a smooth, metallic-appearing coating is obtained which does not spall when subjected to repeated heating and cooling cycles, but does tend to craze. Failure, or break-through of a continuous coating is generally found at the intersection of crazing cracks.

APPENDIX

TORCH-FIRING TEST

A torch-firing test was developed at Battelle as a simple means of screening materials for rocket-motor liners.

In this test, the heat was supplied by a No. 23 automatic torch, equipped with a No. 80N single-flame tip, manufactured by the Harris Calorific Company, Cleveland, Ohio. A mixture of natural gas at 60-psi pressure and oxygen at 90-psi pressure was used.

The nozzle specimen employed in this test is shown in Figure A-1. The specimen was a cylinder 2 inches long by 1-1/2 inches in diameter, and containing a hole, 1 inch in diameter tapered to 1/2 inch in diameter, located symmetrically on the axis of the cylinder.

Figure A-2 is a plan sketch of the test apparatus. For support during the test, the nozzle specimen was mounted centrally in a graphite cylinder, 6 inches in diameter and 2-1/2 inches thick. A 1/4-inch annulus between the outer diameter of the nozzle and the inner diameter of the graphite support was filled with a refractory cement to hold the nozzle in place.

The mounted nozzle specimen and the torch were supported rigidly in a horizontal plane by adjustable clamps. The torch tip was aligned axially with the specimen, allowing about 1/2 inch between the tip and the specimen.

Before testing, the specimen support assembly was rotated 90 degrees about a fixed axis, and the torch was lighted and adjusted to the proper gas pressure and flow. The specimen support assembly then was rotated back to the predetermined position. The recorded time of the test was started the instant the flame passed through the specimen.

The surface temperature of the specimen was determined by an optical pyrometer sighted into the large end of the tapered hole at an angle of about 45 degrees from the axis of the specimen.

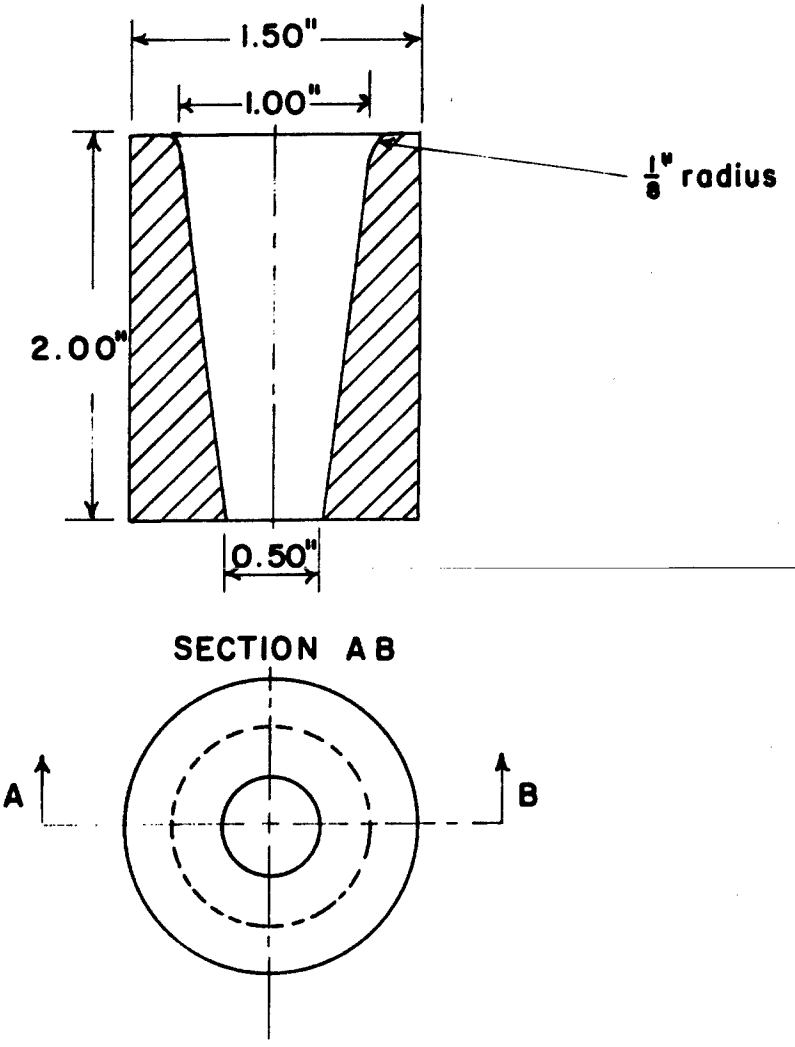
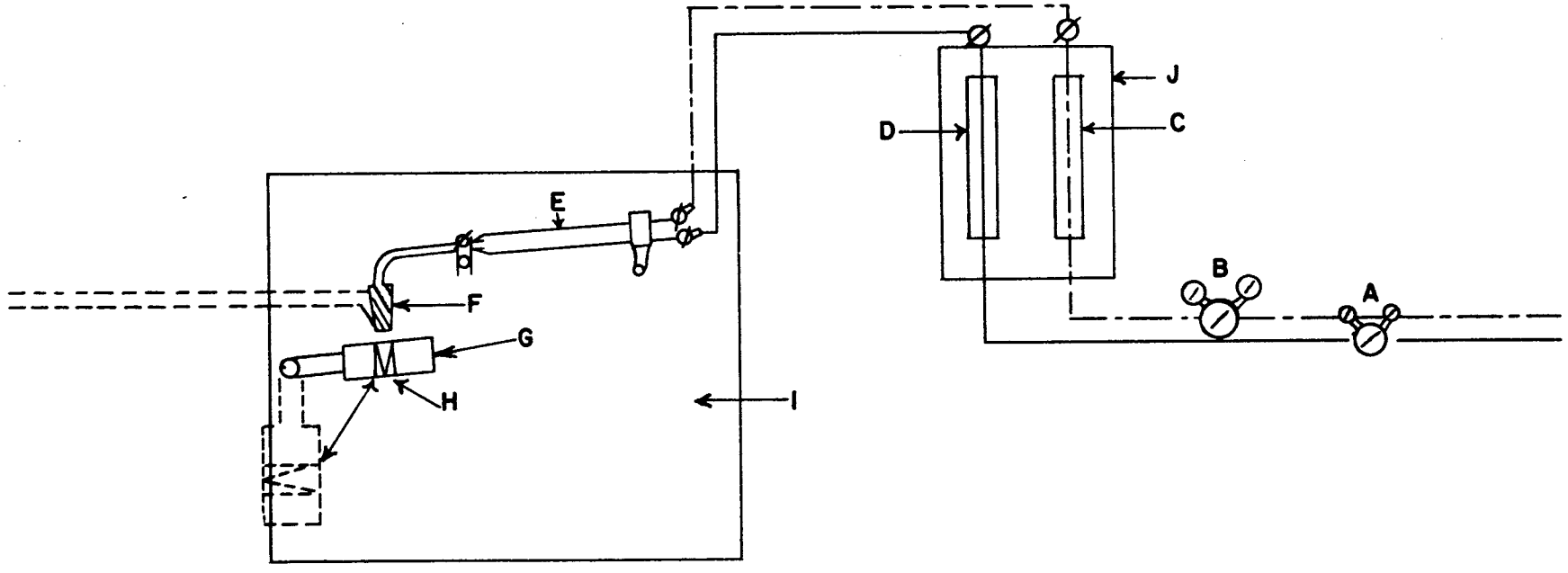


FIGURE A-I. LABORATORY TORCH TEST NOZZLE

A-11931



——— Oxygen supplied by Regulator "A" at 90-psi pressure
— — — Natural gas supplied by Regulator "B" at 60 -psi pressure
- - - - - - - Water supply for cooling coil on Heating Tip "F"

A - Oxygen regulator - National Cylinder Gas Co. - range, 0. 400 psi
B - Gas regulator - National Cylinder Gas Co. - range, 0. 400 psi
C - Fischer Porter Laboratory Flowmeter - Size No. 4 - 1/2 inch - natural gas
D - Fischer Porter Laboratory Flowmeter - Size No. 4 - 1/2 inch - oxygen
E - Oxygen - acetylene mixer handle No. 23 - Harris Calorific Co.
F - Water-cooled single-flame heating tip - No. 80N - Harris Calorific Co.
G - Graphite holder for test specimen
H - Test specimen
I - Table
J - Wall mounting

FIGURE A-2 TORCH-FIRING-TEST APPARATUS

A-11930

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AUTHOR: WADC TR 58-457	
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